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Transport in Porous Media

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Abstract

This paper presents an analytical solution of reactive transport with equilibrium and kinetic reactions. A benchmark model of A $\leftrightarrow$ B $\leftrightarrow$ C $\rightarrow$ chain reactions is developed for the purpose of verifying numerical computer codes and qualifying mathematical models. A reaction matrix is derived for both the equilibrium and first-order kinetic reactions and further decoupled as a diagonal matrix. Therefore, the partial differential equations (PDEs) coupled by the reaction matrix can be transformed into independent PDEs, for which closed-form solutions exist or can be derived. The analytical solution derived in this paper is compared with numerical results.

Key words: Analytical solution, equilibrium, kinetics, transport, reaction.

1. Introduction

Several numerical computer codes have been developed in the past for modeling reactive transport in porous media (e.g., Nitao, 1998; Xu et al., 1998; Clement et al., 1998, 2000). A wide range of reactions at various time scales, such as chemical, biochemical, and geochemical reactions, is coupled in partial differential equations and solved accordingly using ODE (ordinary differential equation) solvers for kinetics and using DAE (differential algebraic equation) solvers for equilibrium reactions. In order to verify and qualify numerical computer codes, appropriate analytical solutions have to be used as references. However, due to the lack of an analytical solution of the transport with both kinetic and equilibrium reactions, numerical codes are only benchmarked by comparing numerical results against analytical solutions with first-order kinetics (Sun and Clement, 1999; Zhang and Woodbury, 2002; Prommer et al., 2003; Zhang et al., 2005). Reactive transport coupled with equilibrium reactions has not yet been qualified. In this paper, we propose a benchmark problem of a sequential equilibrium and first-order kinetic reaction chain and provide a closed-form solution.

2. The Reactive Transport System

We consider here the transport with two-step equilibrium chain reactions and one-step first-order kinetic reaction with the following overall stoichiometry,

$$\mathrm{A} \overset{k_1}{\longleftrightarrow} \mathrm{B} \overset{k_2}{\longleftrightarrow} \mathrm{C} \overset{k_3}{\longrightarrow} . \tag{1}$$

Reactions between A and B, and between B and C are assumed to be reversible and equilibrium, which can be expressed as

$$k_1 = \frac{\overline{B}}{\overline{A}}, \quad k_2 = \frac{\overline{C}}{\overline{B}} \tag{2}$$

where k_1 and k_2 are equilibrium constants (dimensionless), $\overline{A}$, $\overline{B}$, and $\overline{C}$ are the equilibrium concentrations of species A, B, and C, respectively. Besides the equilibrium reactions, species C is also under first-order kinetic reaction,

$$\frac{dC}{dt} = -k_3 C \tag{3}$$

where k_3 is the first-order reaction rate [T^{-1}]. If all reactions are instantaneous, the equilibrium concentrations can be determined as

$$\begin{aligned} \overline{A} &= A - \mathcal{X} \\ \overline{B} &= B + \mathcal{X} - \mathcal{Y} \\ \overline{C} &= C + \mathcal{Y} - k_3 C \end{aligned} \tag{4}$$

where

$$\begin{bmatrix} \mathcal{X} \\ \mathcal{Y} \end{bmatrix} = \frac{1}{\alpha} \begin{bmatrix} k_1 + k_1 k_2 & -1 & -(1-k_3) \\ k_1 k_2 & k_1 k_2 & -(1+k_1)(1-k_3) \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} \tag{5}$$

$$\alpha = 1 + k_1 + k_1 k_2.$$

When the reaction terms are coupled, the partial differential equations of transport are written

$$\begin{aligned} \frac{\partial A}{\partial t} &= \mathcal{L}(A) - \mathcal{X} \\ \frac{\partial B}{\partial t} &= \mathcal{L}(B) + \mathcal{X} - \mathcal{Y} \\ \frac{\partial C}{\partial t} &= \mathcal{L}(C) + \mathcal{Y} - k_3 C, \end{aligned} \tag{6}$$

where $\mathcal{L}$ is the advection-dispersion operator expressed as

$$\mathcal{L}(A) = \nabla \cdot (\nabla \cdot \mathbf{D}A - \mathbf{v}A),$$

and $\mathbf{D}$ [$\mathrm{L}^2\mathrm{T}^{-1}$] is the tensor of dispersion coefficients and $\mathbf{v}$ [LT^{-1}] is the vector of velocity. Reformatting (6), the reactive transport system can be expressed in matrix format

$$\frac{\partial \mathbf{c}}{\partial t} = \mathcal{L}(\mathbf{c}) + \mathbf{F}\mathbf{c}, \quad \mathbf{F} = \frac{1}{\alpha} \begin{bmatrix} -(k_1 + k_1 k_2) & 1 & (1-k_3) \\ k_1 & -(1+k_1 k_2) & k_1(1-k_3) \\ k_1 k_2 & k_1 k_2 & -(1+k_1+k_1 k_2 k_3) \end{bmatrix} \tag{7}$$

where $\mathbf{c} = [A\ B\ C]^T$.

3. An Analytical Solution

The reaction matrix, $\mathbf{F}$, is diagonalized as

$$\mathbf{F} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}, \tag{8}$$

where

$$\mathbf{S} = \begin{bmatrix} 1-k_3 & 0 & 1 \\ 0 & 1-k_3 & k_1 \\ -1 & -1 & k_1k_2 \end{bmatrix}, \quad \mathbf{S}^{-1} = \frac{1}{\gamma}\begin{bmatrix} \frac{\gamma-1}{1-k_3} & -\frac{1}{1-k_3} & -1 \\ \frac{-k_1}{1-k_3} & \frac{\gamma-k_1}{1-k_3} & -k_1 \\ 1 & 1 & 1-k_3 \end{bmatrix},$$

$$\mathbf{\Lambda} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -\frac{k_1k_2k_3}{\alpha} \end{bmatrix}, \quad \gamma = \alpha - k_1k_2k_3. \tag{9}$$

Substituting (8) into (7) and multiplying by $\mathbf{S}^{-1}$ yield

$$\frac{\partial \mathbf{a}}{\partial t} = \mathcal{L}(\mathbf{a}) + \mathbf{\Lambda}\mathbf{a}, \qquad \mathbf{a} = \mathbf{S}^{-1}\mathbf{c}. \tag{10}$$

In terms of concentration $\mathbf{a}$, each PDE in (10) is independent of other two PDEs. The reaction terms are decoupled in the "a" domain. Thus, we can write

$$a_i = f_i(x,t,\lambda_i), \quad \forall i = 1,2,3, \tag{11}$$

where $\mathbf{\Lambda} = -\text{diag}([\lambda_1 \ \lambda_2 \ \lambda_3])$, and $\lambda_1 = \lambda_2 = 1$ and $\lambda_3 = k_1k_2k_3/\alpha$. For example, the analytical solution of Bear (1979, p.~268) can be applied to the transport in a semi-infinite column:

$$f_i(x,t) = \frac{a_i^o}{2}\exp\left(\frac{vx}{2D}\right)\left[\exp(-\beta_i x)\text{erfc}\gamma_i^- + \exp(\beta_i x)\text{erfc}\gamma_i^+\right], \tag{12}$$

where

$$\beta_i = \left(\frac{v^2}{4D^2} + \frac{\lambda_i}{D}\right)^{1/2}, \quad \text{erfc}(\eta) = 1 - \text{erf}(\eta) = \frac{2}{\sqrt{\pi}}\int_\eta^\infty \exp(-\tau^2)d\tau,$$

$$\gamma_i^- = \frac{x - (v + 4\lambda_i D)^{1/2}t}{2(Dt)^{1/2}}, \quad \gamma_i^+ = \frac{x + (v + 4\lambda_i D)^{1/2}t}{2(Dt)^{1/2}}, \quad i = 1,2,3.$$

Finally, the closed-form solution is derived as $\mathbf{c} = \mathbf{S}\mathbf{a}$.

4. Application

As a demonstration of the analytical solution, we consider the transport of the three reactive species in a one-dimensional system. Both analytical and numerical solutions (using RT3D, Clement et al., 1998) are computed along the one-dimensional column of 40 meters discretized using 40 evenly spaced elements. The boundary condition assumed is the same as that used in deriving the basic analytical solution (12). The dispersion coefficient and velocity are assumed to be 0.4 m^2d^{-1} and 0.5 md^{-1}, respectively. The equilibrium constants k_1 and k_2 are assumed to be 1.5 and 2.0, and the first-order reaction rate, k_3, is 0.02 d^{-1}.

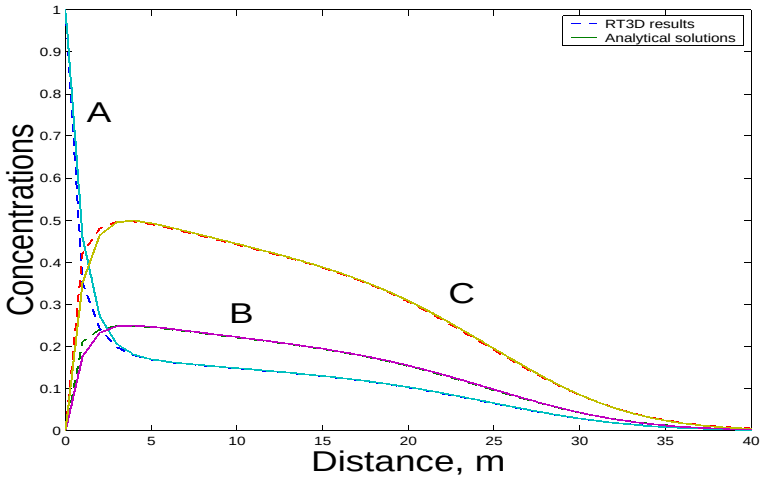

Figure 1. Comparison of analytical solutions against RT3D results at 50 days.

The computations were performed using MATLAB 6.1.0.450 (R12.1) on SunBlade 100. The CPU time required for running the RT3D was 349.18 seconds while that required for the analytical solution derived was 0.0118 seconds. As compared in Figure 1, the solution can be considered identical to the numerical one although the analytical solution requires less CPU time.

With the analytical solution derived, we compute the snapshot concentration profiles of species A, B, and C at 10, 20, 50, and 100 days as shown in Figure 2.

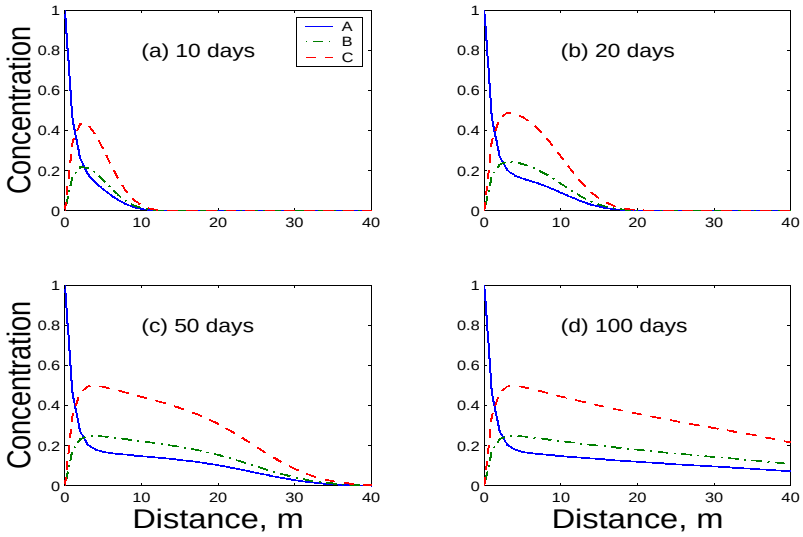

Figure 2. Concentration profiles at 10, 20, 50, and 100 days.

When $t \Rightarrow \infty$, the long-time behavior of the solution can be demonstrated by replacing (12) with

$$f_i(x,\infty) = a_i^o \exp\left[\left(\frac{v}{2D} - \beta_i\right) x\right], \quad \forall i = 1,2,3. \tag{13}$$

Then, the steady-state solution is expressed as

$$c_1(x,\infty) = \frac{\gamma - 1}{\gamma} \exp\left[\left(\frac{v}{2D} - \beta_1\right) x\right] + \frac{1}{\gamma} \exp\left[\left(\frac{v}{2D} - \beta_3\right) x\right]$$

$$c_2(x,\infty) = -\frac{k_1}{\gamma}\left\{\exp\left[\left(\frac{v}{2D}-\beta_2\right)x\right] - \exp\left[\left(\frac{v}{2D}-\beta_3\right)x\right]\right\}$$

$$c_3(x,\infty) = \frac{1}{\gamma}\left\{\frac{1-\gamma}{1-k_3}\exp\left[\left(\frac{v}{2D}-\beta_1\right)x\right] + \frac{k_1}{1-k_3}\exp\left[\left(\frac{v}{2D}-\beta_2\right)x\right]\right.$$

$$\left. + k_1 k_2 \exp\left[\left(\frac{v}{2D}-\beta_3\right)x\right]\right\}. \tag{14}$$

The steady-state concentration profiles of the three species for the given parameters are shown in Figure 3.

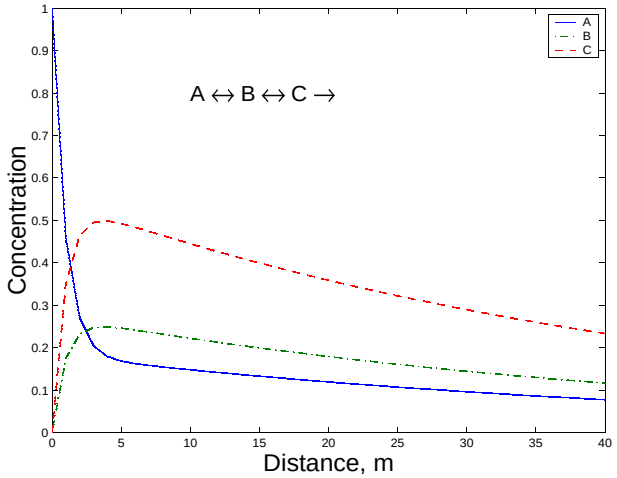

Figure 3. Steady-state concentration profiles of species A, B, and C when $k_1 = 1.5$, $k_2 = 2.0$, and $k_3 = 0.02$.

When $k_3 = 0$ (the first-order kinetics reaction stops), the analytical solution is simplified as one of transport with two-step equilibrium reactions. Correspondingly, the steady state concentration profiles are shown in Figure 4.

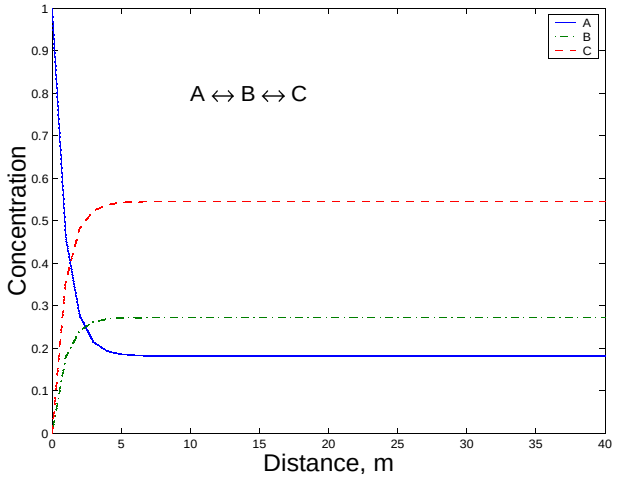

Figure 4. Steady-state concentration profiles of species A, B, and C when $k_1 = 1.5$, $k_2 = 2.0$, and $k_3 = 0.0$.

Figure 4 indicates that all three species reach constant concentrations, 0.1818, 0.2727, 0.5455, respectively, when $x \geq 5.0$ m. The sensitivity of constant species concentrations to the equilibrium constants, k_1 and k_2, is shown in Figure 5.

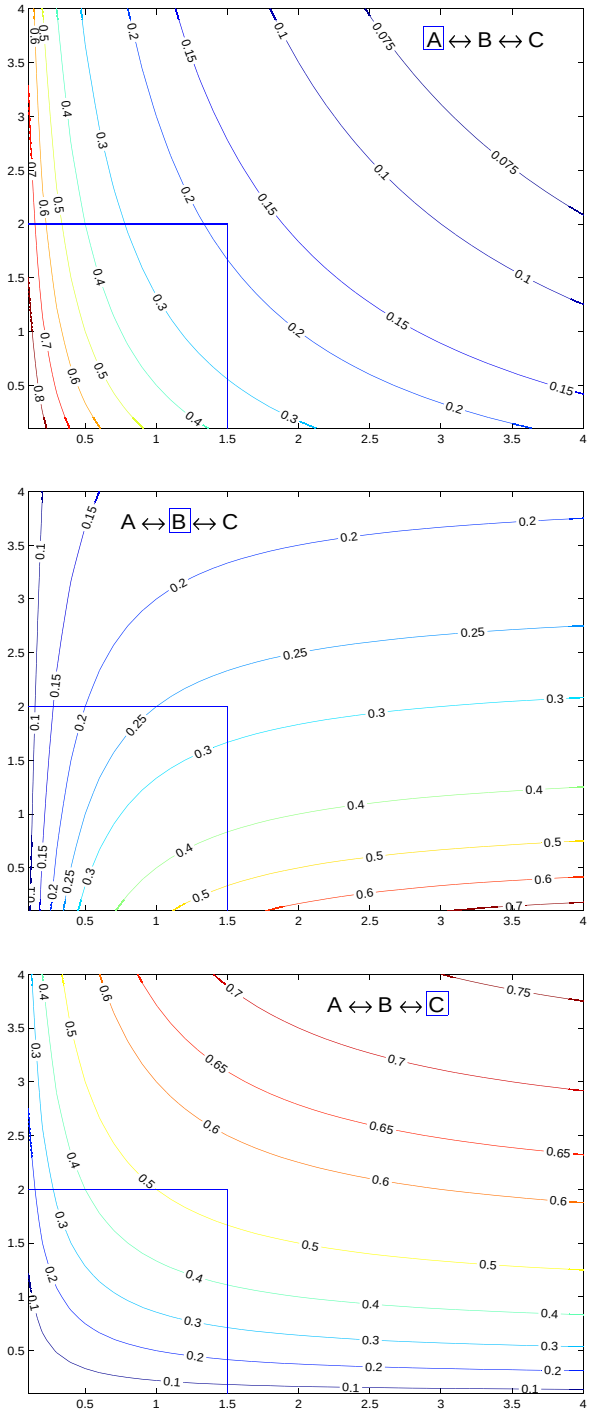

Figure 5. Sensitivity of steady-state concentration profiles of species A, B, and C to equilibrium constants, k_1 and k_2 when $k_3 = 0.0$.

5. Conclusions

An exact solution is presented for transport in porous media with sequential equilibrium and first-order kinetic reactions. In order to verify functionalities of numerical computer codes for reactive transport with both equilibrium and kinetic reactions, a benchmark model of A $\leftrightarrow$ B $\leftrightarrow$ C$\rightarrow$ is provided to cover reversible and irreversible, equilibrium and kinetic reactions. The solution of Bear (1979, p.$\sim$268) is used as an example of basic solution (Eq. (12)) in the solution scheme for the given initial and boundary conditions. However, the transform matrices derived in this paper for the coupled reactions are applicable to any other initial/boundary condition if the corresponding solution for a single species is available. This paper not only provides the exact solution for transport with coupled equilibrium/kinetic reactions, but also offers a framework for deriving more closed form solutions under various initial/boundary conditions. For this reason, we recommend that numerical computer codes of reactive transport be verified using this benchmark model solution.

Appendix A: Mass Balance Equation of Species A

In this appendix, we demonstrate that the derived solution satisfies the mass balance equation. For the purpose of simplicity, we use the steady-state solution in (14) to demonstrate $\mathcal{L}(c_1) - \mathcal{X} = 0$.

Let

$$\xi_i = \frac{v}{2D} - \beta_i, \quad \eta_i = \exp\left[\left(\frac{v}{2D} - \beta_i\right) x\right] = \exp\left(\xi_i x\right). \tag{15}$$

Then,

$$c_1 = \frac{\gamma - 1}{\gamma}\eta_1 + \frac{1}{\gamma}\eta_3 \tag{16}$$

The first- and second-order derivatives of species A are

$$\frac{\partial c_1}{\partial x} = \frac{\gamma - 1}{\gamma}\xi_1\eta_1 + \frac{1}{\gamma}\xi_3\eta_3, \tag{17}$$

$$\frac{\partial^2 c_1}{\partial x^2} = \frac{\gamma - 1}{\gamma}\xi_1^2\eta_1 + \frac{1}{\gamma}\xi_3^2\eta_3. \tag{18}$$

The advective-dispersive flux is expressed

$$\mathcal{L}(c_1) = D\frac{\partial^2 c_1}{\partial x^2} - v\frac{\partial c_1}{\partial x} = D\frac{\gamma - 1}{\gamma}\xi_1^2\eta_1 + \frac{D}{\gamma}\xi_3^2\eta_3 - v\frac{\gamma - 1}{\gamma}\xi_1\eta_1 - \frac{v}{\gamma}\xi_3\eta_3.$$

$$= \frac{\gamma - 1}{\gamma}\overbrace{\left(D\xi_1^2 - v\xi_1\right)}^{(a)}\eta_1 + \frac{1}{\gamma}\underbrace{\left(D\xi_3^2 - v\xi_3\right)}_{(b)}\eta_3 \tag{19}$$

On the other hand, using (5), the reaction term $\mathcal{X}$ can be written as

$$\mathcal{X} = \frac{\gamma - 1}{\gamma}\eta_1 + \frac{1}{\gamma}\frac{k_1 k_2 k_3}{\alpha}\eta_3. \tag{20}$$

In order to conserve the mass balance equation of species A, terms (a) and (b) in Equation (19) should be

$$D\xi_1^2 - v\xi_1 = 1, \tag{21}$$

and

$$D\xi_3^2 - v\xi_3 = \frac{k_1 k_2 k_3}{\alpha}. \tag{22}$$

Since

$$\lambda_1 = 1, \quad \beta_1 = \left(\frac{v^2}{4D^2} + \frac{\lambda_1}{D}\right)^{1/2} = \left(\frac{v^2}{4D^2} + \frac{1}{D}\right)^{1/2}, \tag{23}$$

we have

$$\begin{aligned} D\xi_1^2 - v\xi_1 &= D\xi_1\left(\xi_1 - \frac{v}{D}\right) = \left(\beta_1 - \frac{v}{2D}\right)\left(\beta_1 D + \frac{v}{2}\right) \\ &= D\left(\beta_1^2 - \frac{v^2}{4D^2}\right) = D\left(\frac{1}{D}\right)1. \end{aligned} \tag{24}$$

Therefore, (21) holds.

Similarly,

$$\lambda_3 = \frac{k_1 k_2 k_3}{\alpha}, \quad \beta_3 = \left(\frac{v^2}{4D^2} + \frac{\lambda_3}{D}\right)^{1/2} = \left(\frac{v^2}{4D^2} + \frac{k_1 k_2 k_3}{\alpha D}\right)^{1/2} \tag{25}$$

hence

$$\begin{aligned} D\xi_3^2 - v\xi_3 &= \xi_3\left(D\xi_3 - v\right) = \left(\beta_3 - \frac{v}{2D}\right)\left(D\beta_3 + \frac{v}{2}\right) = D\left(\beta_3^2 - \frac{v^2}{4D^2}\right). \\ &= D\left(\frac{k_1 k_2 k_3}{\alpha D}\right) = \frac{k_1 k_2 k_3}{\alpha}. \end{aligned} \tag{26}$$

Thus, (22) is proved.

Substituting (24) and (26) into (19) for terms (a) and (b),

$$\mathcal{L}(c_1) = \mathcal{X}. \tag{27}$$

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